

APPENDIX B

**(VERSION OF SUBSTITUTE SPECIFICATION EXCLUDING CLAIMS
WITH MARKINGS TO SHOW CHANGES MADE)**

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APPLICATION FOR LETTERS PATENT

for

LOW HUMIDITY UPTAKE SOLID PYROTECHNIC COMPOSITIONS,
AND METHODS FOR MAKING THE SAME

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TITLE OF THE INVENTION

LOW HUMIDITY UPTAKE SOLID PYROTECHNIC COMPOSITIONS, AND METHODS FOR MAKING THE SAME

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of United States Provisional Application No. 60/261,111 filed in the U.S. Patent & Trademark Office on January 12, 2001, the complete disclosure of which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0002] Field of the Invention: The present invention is directed to solid pyrotechnic compositions, including novel black powder substitute and boron/potassium nitrate substitute compositions. The present invention is also directed to methods for making the solid pyrotechnic compositions.

2. Description of the Related Art

[0003] State of the Art: Black powder and boron/potassium nitrate (B/KNO_3) are two classic igniter formulations with broad current usage in a wide variety of applications. Black powder is composed of 72-75 weight percent potassium nitrate, 15-18 weight percent charcoal, and 10 weight percent sulfur. Variations in this basic black powder formulation are known. The optimum formulation for black powder is generally accepted to consist of 75 weight percent potassium nitrate, 15 weight percent charcoal, and 10 weight percent sulfur. Black powder of this formulation has a predicted flame temperature of 1950K at 1000 psi. Boron/potassium nitrate, on the other hand, in its optimum formulation is composed of 75 weight percent potassium nitrate and 25 weight percent boron. Compared to black powder, boron/potassium nitrate has a significantly higher flame temperature of 3034K at 1000 psi.

[0004] Because the flame temperatures of black powder and boron/potassium nitrate differ significantly, the applications in which these igniter compositions are used somewhat differ. Black powder is by far the less expensive of the two compositions, has a cooler flame temperature, and produces less slag than boron/potassium nitrate. For these reasons, black powder

is often chosen over boron/potassium nitrate in the ignition trains of multiple-use hardware, including guns of various sizes and applications. Boron/potassium nitrate is usually utilized in applications where a higher flame temperature is critical for rapid and reproducible ignition. For example, common applications for B/KNO₃ include ignition trains for rockets, decoy flares, and gas generators of automotive secondary safety restraints or “air bag” devices. Boron/potassium nitrate is not, however, used as often in multi-use hardware due to the expense of ~~BKNO₃~~^{B/KNO₃} and the high ~~BKNO₃~~^{B/KNO₃} flame temperature, which may cause premature erosion of reusable hardware.

[0005] Processes are known in the art for making black powder. For example, charcoal and sulfur may be ball milled together into an intimate mixture for feeding into an extruder. Ball milling also serves to reduce the particle size of the charcoal. Potassium nitrate is dried and likewise processed through a rod mill to reduce the average particle size to about 50 microns. Graphite may optionally be introduced into the rod mill for the purpose of reducing electrostatic discharge sensitivity (ESD). The milled charcoal, sulfur, and potassium nitrate, and optionally the graphite, are then compounded in accordance with ~~well known~~^{well-known} methods.

[0006] The combustion of black powder produces a plethora of effluents. It has been calculated that the black powder combustion generates significant amounts of carbon monoxide, sulfur dioxide, and hydrogen sulfide. Potassium sulfide has been predicted to constitute over 20 percent of the combustion products. At flame temperature, potassium sulfide is produced in the liquid state,~~state~~ and is likely to undergo after-burning with atmospheric oxygen to produce copious amounts of sulfur dioxide. The carbon monoxide and hydrogen sulfide are also susceptible to after-burning, yielding carbon dioxide and sulfur dioxide, respectively.

[0007] Sulfur dioxide is extremely destructive to tissue of the mucous membranes and upper respiratory tract, eyes, and skin. Inhalation may result in spasm, inflammation, and edema of the larynx and bronchi, chemical pneumonitis, and pulmonary edema. Thus, exposure to sulfur dioxide can lead to a series of health problems and, in the case of extended exposure, death.

[0008] The charcoal constituent of black powder imparts a degree of unpredictability to the performance of the igniter composition. Charcoal is produced by carbonization of wood. As described in U.S. Patent No. 5,320,691, the chemical and physical properties of wood vary greatly, depending upon the particular properties of the tree species, soil composition, and environmental conditions from which the wood is taken. Due to inherent variability of wood and fluctuations in

the carbonization process, the properties of charcoal tend to vary from batch to batch. These variations can affect the consistency of black powder performance.

[0009] Another problem associated with black powder is its hygroscopicity. Black powder absorbs about 1.5 weight percent moisture under 75 percent relative humidity at a temperature of 21.1°C (70°F) over the period of 24 hours. If black powder picks up sufficient moisture, there is a possibility that the black powder will not burn as fast. Hence, an igniter or other device comprising the black powder might not perform up to specification in a high relative humidity. Also, concerns have been expressed that water will cause the potassium nitrate to migrate out of the black powder pellet and cause corrosion of metallic parts of the device.

[0010] A black powder substitute composition is described in U.S. Patent No. 5,320,691 to Weber. This composition is a dispersion of phenolphthalein, potassium nitrate, and sulfur in a binding phase of phenolphthalein salt. Phenolphthalein is the reaction product of a phenolic compound and phthalic anhydride. The cations of the phenolphthalein salt are selected from the group consisting of sodium, potassium, lithium, and ammonium. Phenolphthalein salt (optionally in combination with organic phenolphthalein) is used because of the ballistic enhancement that the phenolphthalein salt imparts in comparison to organic phenolphthalein. Although the substitution of phenolphthalein salt for charcoal obviates the predictability problems raised by the charcoal of the conventional black powder composition, sulfur remains as a requisite ingredient of the substitute composition. Thus, the black powder substitute of U.S. Patent No. 5,320,691 does not address the above-mentioned problems associated with sulfur and sulfur dioxide production. Also, phenolphthalein salts are hygroscopic,hygroscopic and do not overcome concerns of moisture uptake.

[0011] Another black powder substitute composition is described in U.S. Patent & Trademark Office document H72 to Wise, et al. The solid pyrotechnic composition contains 75 weight percent potassium nitrate, 10 weight percent elemental sulfur, and 15 weight percent crystalline compound. The crystalline compound may be fluorescein, phenolphthalein, 1,5-naphthalenediol, anthraflavic acid, terephthalic acid, and alkali metal salts thereof. As in the case of other known black powder substitute compositions, H72 relies on elemental sulfur for minimizing the ignition delay of the igniter.

BRIEF SUMMARY AND OBJECTS OF THE INVENTION

[0012] It is to be noted that, as used in the specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, by way of example, the term "an organic crystalline compound" includes in its definition not only a single organic crystalline ~~compound, compound~~ but also a combination of two or more organic crystalline compounds.

[0013] The term "polymer" encompasses homopolymers, copolymers, and terpolymers. ~~Terpolymer~~"Terpolymer" means a polymer made from three or more monomers.

[0014] As used herein, the term "organic crystalline compound" means an organic compound that is not present as a salt, unless the term in the context clearly dictates otherwise.

[0015] As used herein, the term "a salt of an organic crystalline compound" means a negatively charged organic compound ionically bonded to a metal cation or ammonium cation to counterbalance the negative charge of the organic compound. An example is dipotassium phenolphthalein.

[0016] ~~It is an object of the~~The present invention ~~to provide~~provides a solid pyrotechnic composition having a flame temperature and exhibiting ballistic performance comparable to that of black powder, but which is preferably (but not necessarily) formulated to contain neither charcoal nor sulfur.

[0017] In accordance with one aspect of the invention, a solid pyrotechnic composition constituting a black powder substitute is provided ~~for attaining the above and other objects~~. The composition comprises about 40 weight percent to about 90 weight percent oxidizer particles having a mean particle size of not greater than about 30 microns. The oxidizer particles comprise (a) at least one member selected from the group consisting of alkali metal nitrate and ammonium nitrate and (b) at least one member selected from the group consisting of alkali metal perchlorate and ammonium perchlorate. The preferred alkali metal is potassium. The solid pyrotechnic composition further comprises organic crystalline particles ~~and optionally~~and, optionally, salts of organic crystalline particles. The organic crystalline particles and the optional salts of organic crystalline particles preferably have a mean particle size of not greater than about 30 microns and preferably account for about 10 weight percent to about 60 weight percent of the total weight of the

solid pyrotechnic composition. The organic crystalline particles preferably comprise phenolphthalein.

[0018] ~~It is an object of the~~The present invention, according to a second aspect to provideaspects, provides a solid pyrotechnic composition that has a flame temperature and exhibits ballistic performance comparable to that of boron/potassium nitrate, and that is preferably (although not necessarily) free of boron.

[0019] In accordance with this second aspect of the invention, a solid pyrotechnic composition comprising a boron/potassium nitrate substitute is provided for attaining the immediately above-mentioned object and other objects. The composition comprises about 40 weight percent to about 90 weight percent oxidizer particles having a mean particle size of not greater than about 30 microns. The oxidizer particles comprise at least one member selected from the group consisting of alkali metal perchlorate and ammonium perchlorate. The perchlorate particles make up from about 20 weight percent to about 90 weight percent of the total weight of the composition, and more preferably 30 weight percent to 90 weight percent of the total weight of the composition. The oxidizer particles may also comprise other materials, including at least one member selected from the group consisting of alkali metal nitrate and ammonium nitrate. The preferred alkali metal for the perchlorate and nitrate is potassium. The solid pyrotechnic composition further comprises organic crystalline particles ~~and optionally~~and, optionally, salts of organic crystalline particles. The organic crystalline particles and the optional salts of organic crystalline particles preferably have a mean particle size of not greater than 30 microns and preferably account for about 10 weight percent to about 60 weight percent of the total weight of the solid pyrotechnic composition. The organic crystalline particles are preferably phenolphthalein.

[0020] In their respective preferred embodiments, the selection of the ingredients of these novel black powder and B/KNO₃ substitute compositions can significantly reduce the production of harmful effluents derived from sulfur. In this way, the invention can provide an improvement in the environmental impact and worker health risks encountered during firing and conducting post-fire clean-up operations of articles using the compositions. Additionally, the solid pyrotechnic composition according to presently preferred embodiments may possess excellent impact and thermal sensitivities, thereby reducing the incipient hazards of the igniter to detonation and premature ignition via response to stimuli such as impact, friction, heat, and/or electrostatic

discharge. Further, the use of organic crystalline compounds in lieu of (or partial lieu of) crystalline salts, as well as the use of ~~non hygroscopic~~nonhygroscopic binders, can significantly lower the moisture uptake or absorption of the inventive solid pyrotechnic composition in comparison to black powder. Furthermore, the omission of charcoal from preferred embodiments of the invention can improve upon the reproducibility and uniformity of the ballistic properties of the pyrotechnic composition, as well as minimize moisture uptake of the composition.

[0021] ~~It is yet another object of this invention~~The present invention, according to a third aspect of the ~~invention to provide~~invention, provides a novel method of making black powder substitute and boron/potassium nitrate.

[0022] In accordance with the principles of this third aspect of the invention, the above-mentioned object and other objects are attained by a process in which an alkali metal hydroxide is combined with at least one organic crystalline compound to produce a solution comprising a salt of the organic crystalline compound. The organic crystalline compound is preferably selected from the group consisting of phenolphthalein and a compound derived from reaction between a phenolic compound and phthalic anhydride. The solution is then combined with at least one acid selected from the group consisting of nitric acid and perchloric acid. The alkali metal hydroxide reacts with the nitric acid or perchloric acid to form alkali metal nitrate particles or alkali metal perchlorate particles, respectively. Additionally, the acid serves to convert the salt back to the organic crystalline compound, while reducing the particle size of the organic crystalline compound to not greater than about 30 microns. Additional ~~oxidizers~~oxidizer particles having a mean particle size of not greater than about 30 microns may be added. The additional oxidizer particles comprise a perchlorate salt and/or a nitrate salt. The pyrotechnic composition may then be dried, if necessary or desired.

[0023] Additional ~~objects and~~advantages of the invention will be set forth in the description that follows, and in part will be apparent from the description, or may be learned by practice of the invention. The ~~objects and~~advantages of the invention may be realized and obtained by means of the instrumentalities and combinations pointed out in the appended claims.

BRIEF DESCRIPTION OF THE DRAWING

[0024] The accompanying drawing, which is incorporated in and constitutes a part of the specification, illustrates a comparison of igniter performance of a commercially utilized B/KNO₃ igniter and a boron-free igniter of Example 15 prepared in accordance with the present invention. The drawing, together with the general description given above and the detailed description of the preferred embodiments and methods given below, ~~serves~~ to explain the principles of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0025] According to a presently preferred embodiment of the invention, a black powder substitute pyrotechnic composition is provided that comprises oxidizer particles and organic crystalline particles.

[0026] The oxidizer particles according to this embodiment constitute from about 40 weight percent to about 90 weight percent, more preferably 65 weight percent to 80 weight percent, of the total weight of the solid pyrotechnic composition. The mean particle size of the oxidizer particles is not greater than about 30 microns, preferably is not greater than 20 microns, and more preferably is in a range of 5 microns to 20 microns.

[0027] The oxidizer particles of this embodiment comprise at least one nitrate salt. The nitrate salt is preferably at least one member selected from the group consisting of alkali metal nitrate and ammonium nitrate. Exemplary alkali metal nitrates are potassium nitrate, cesium nitrate, rubidium nitrate, and ammonium nitrate, with potassium nitrate being preferred.

[0028] The oxidizer particles of this embodiment also comprise at least one perchlorate salt. The perchlorate salt is preferably at least one member selected from the group consisting of potassium perchlorate and ammonium perchlorate, with potassium perchlorate being preferred. When used in the preferred particulate sizes of about 30 microns or less, the perchlorate salt can be instrumental in permitting the omission of sulfur from the pyrotechnic composition without sacrificing ballistic performance. Upon ignition of the solid pyrotechnic composition, the perchlorate salt can decrease ignition delay of the pyrotechnic composition while increasing pressure rise. It is preferred that 0.5 weight percent to 30 weight percent of the total weight of the

solid pyrotechnic composition consist of the perchlorate salt. More preferably, 5 to 20 weight percent of the solid pyrotechnic composition consists of the perchlorate salt.

[0029] The organic crystalline particles of this embodiment, as well as optionally present salts of the organic crystalline particles, account for about 10 weight percent to about 60 weight, more preferably 13 weight percent to 22 weight percent, of the total weight of the solid pyrotechnic composition. If a salt is present, it is preferred that at least 50 weight percent, more preferably at least 80 weight percent, and still more preferably at least 90 weight percent of the organic crystalline compound be present in a salt-free state. It is possible, and preferred, to use the organic crystalline particles alone, so that the solid pyrotechnic composition is free of any salts of organic crystalline compounds. Although the organic crystalline particles and its optional salts may have mean particle sizes as large as 100 microns, they preferably have a mean particle size of sizes not greater than about 30 microns, more preferably not greater than 20 microns, still more preferably not greater than 15 microns, and still more preferably not greater than 10 microns.

[0030] Preferably, the organic crystalline particles comprise at least one member selected from the group consisting of phenolphthalein and an organic crystalline compound derived from a reaction between a phenolic compound and phthalic anhydride. By way of example, one or more of the 2-6 positions on the phenolic compound and/or one or more of the 2-5 positions on the phthalic anhydride compound can be substituted with functional groups such as -R, -NH₂, -NR¹H, -NR¹R², -NO₂, -OR, and the like, in which R, R¹, and R² are independently selected from, for example, alkyls and aryls.

[0031] The solid pyrotechnic composition of this invention is not limited to phenolphthalein and its derivatives. Instead, other organic crystalline compounds known in the art and those yet to be discovered may also be used. Representative organic crystalline compounds that may be of use with the present invention are described in U.S. Patent & Trademark Office document H72 to Wise, et al. and include fluorescein, 1,5-naphthalenediol, anthraflavic acid, and terephthalic acid.

[0032] The solid pyrotechnic composition of this invention may optionally contain additional ingredients, including non-hygroscopic polymeric binders, for example. Suitable non-hygroscopic polymeric binders that may be used with this embodiment of the invention include those that uptake (*i.e.*, absorb) less than 4% moisture at 75% RH (21.1°C)

~~(70°F))~~ relative humidity at a temperature of 21.1°C (70°F) over 24 hrs. Representative binders include: poly(vinyl acetate), poly(vinyl acetate-co-vinyl alcohol), nylon, poly(ethylene-co-vinyl acetate), polyethylene glycol, alkyl cellulose (e.g., ethyl cellulose), nitrocellulose, certain chain-extended oxetanes (e.g., polyBAMO), glycidyl azide polymer (GAP), and related polymers. Suitable solvent may be used in the process for dissolving the binder and lowering viscosity during production. For example, ethyl acetate is a suitable solvent for poly(vinyl acetate). In the event that the composition is free of polymeric binder, water may be used to facilitate mixing. By way of example and not necessarily limitation, the binders may be present in the composition in a concentration of not more than about 10 weight percent, preferably 3 weight percent to 6 weight percent.

[0033] Other ingredients are also permitted, including graphite, metal or metalloid fuels, and fillers, as desired or needed for the intended application of the solid pyrotechnic composition.

[0034] Compared to conventional black powder, the use of a ~~non-hygroscopic~~ nonhygroscopic binder and the organic crystalline compound ~~lower~~lowers the moisture uptake of the solid pyrotechnic composition of this invention. In preferred embodiments, the moisture uptake of the solid pyrotechnic composition is not greater than 0.3 weight percent, more preferably not greater than 0.25 weight percent, at 75 percent relative humidity ~~and at a temperature of~~ 21.1°C (70°F) over a period of 24 hours.

[0035] Additionally, by adjusting the proportions of oxidizer salts and organic crystalline compound, it is possible to obtain a formulation having, upon ignition, a theoretical flame temperature not greater than 2300K, preferably 1750K to 2300K. Generally, increasing the concentration of perchlorate salt will raise the flame temperature, whereas decreasing the concentration of perchlorate salt will lower the theoretical flame temperature. On the other hand, the theoretical flame temperature has an inverse relationship with the organic crystalline compound. The theoretical flame temperature is calculated by NASA-Lewis thermochemical calculations. A copy of this program is available through NASA Glenn Research Center, Cleveland, Ohio.

[0036] In a currently preferred embodiment of the invention, the black powder substitute (BPS) composition comprises 61.6 weight percent 15 micron potassium nitrate, 15 weight percent 20 micron potassium perchlorate, 18.9 weight percent 6 micron phenolphthalein, and 4.5 weight percent 500,000 MW poly(vinyl acetate).

[0037] In accordance with another embodiment of the invention, a B/KNO₃ substitute pyrotechnic composition is provided that comprises perchlorate salt oxidizer particles and organic crystalline particles.

[0038] Suitable perchlorate salts and organic crystalline particles for this embodiment of the invention can be selected from those described above and listed in connection with the black powder substitute composition. Generally, boron/potassium nitrate burns at a relatively high theoretical flame temperature, preferably at least 2300K, and more preferably in a range of 2300K to 3000K. It is possible to obtain such high flame temperature by using a relatively high perchlorate salt loading, such as about 20 weight percent to about 90 weight percent, more preferably 30 weight percent to 90 weight percent, based on the total weight of the solid pyrotechnic composition. It has been found that perchlorate salts have a greater effect on raising theoretical flame temperature than other oxidizers such as nitrate salts. Generally, in order to regulate theoretical flame temperature, lower loadings of perchlorate salt will be accompanied by high loadings of other oxidizers (e.g., nitrates) relative to organic crystalline compound and optional binder. On the other hand, higher loadings of perchlorate salt will be accompanied by low loadings of other oxidizers relative to organic crystalline compound and optional binder.

[0039] Conventional methods for making black powder and boron/potassium nitrate compositions may be practiced to prepare the solid pyrotechnic composition of this invention. For example, a twin-screw extruder, as described in U.S. Patent No. 5,670,098 to Dillehay et al., may be utilized. Similarly, ball milling, muller milling, and other milling techniques may be used. These methods are well known in the art and described in literature.

[0040] According to one exemplary method contemplated for use with the present invention, the binder is dissolved in a suitable solvent in a Hobart mixer, and the organic crystalline particles (e.g., phenolphthalein) are then added to the dissolved binder. Next, the oxidizer particles are added into the Hobart mixer. The oxidizer particles may be added simultaneously or at different times from each other. If more than one type of oxidizer particles are used, the particles do not have to be premixed. The ingredients are blended in the Hobart mixer as the solvent is removed, such as by vacuum or evaporation, until the material is prilled. The prills are granulated to a suitable size, for example, with a Stokes Granulator. The granules are then dried under appropriate conditions, such as on aluminum trays in a convection oven at 135°F. After drying,

additional granulation may be conducted to break up agglomerates. This technique is merely exemplary. Many modifications may be made to this technique. For example, the binder may be ~~pre-blended~~preblended with the organic crystalline particles prior to adding the solvent. Similar conditions and steps may be used for processing with a twin-screw extruder.

[0041] Optionally, if the granules are to be pressed into pellets, blending of the granules with a suitable processing aid, such as calcium stearate, may be performed. Preferably, the calcium stearate coating constitutes about 0.5 weight percent of the particles. Pellets may be used as is, or may be further processed, such as by grinding, to make high density granules having ballistics comparable ~~ballistics~~ to granulated black powder.

[0042] In a preferred aspect of the method of the invention, an alkali metal hydroxide, such as potassium hydroxide, is combined with at least one organic crystalline compound, such as phenolphthalein or a phenolphthalein derivative, to produce a solution comprising a salt of the organic crystalline compound. The solution is combined with nitric acid or perchloric acid, ~~or~~or, if ~~desired~~desired, a combination of the acids. The alkali metal hydroxide reacts with the nitric acid or perchloric acid to form alkali metal nitrate particles or alkali metal perchlorate particles, respectively. Additionally, the acid serves to convert the salt back to the organic crystalline compound, while preferably reducing the particle size of the organic crystalline compound to not greater than about 30 microns, preferably not greater than 20 microns. Additional ~~oxidizers~~oxidizer particles having a mean particle size of not greater than about 30 microns may be added. This addition or combination step may be performed ~~in situ~~in situ by reaction of the alkali metal hydroxide with the nitric or perchloric acid to form the oxidizer particles. Thus, the oxidizer particles comprise a nitrate salt and/or a perchlorate salt. The pyrotechnic composition may then be dried, if necessary or desired. By way of example and without limitation, drying may be conducted under vacuum or at atmospheric ~~pressure~~pressure and may be conducted at room or elevated temperatures. Drying methods are well known in the art.

[0043] Determination of mean particle size is performed in accordance with standard ISO-13320-1:1999(E) "Particle Size Analysis-Laser Diffraction Methods",Methods, the disclosure of which is incorporated herein by express reference. Generally, this standard describes deriving mean particle size from a matrix conversion of angular light scattering intensity measurements as a function of scattering angle and wavelength of light. Suitable algorithms are based on the

Fraunhauffer forward light scattering ~~theory~~theory, which incorporates the refractive indices of both the same and the carrier medium.

[0044] With a MICROTAC® system, a recirculating bath is used to present a suspended stream of particles to the instrument's optical cell. Inside the cell, the suspended stream of particles is impinged by a small laser beam~~beam~~, creating a diffraction pattern of light. This diffraction pattern of light is converted into an energy distribution matrix which yields the various particle size properties such as intensity, distribution, mean diameter, cumulative volume, and so forth for the given sample.

[0045] The solid pyrotechnic compositions of this invention are useful for various applications, including, by way of example, as initiators, first fire compositions used with hot wires, gas generants, propellants, and the like. The solid pyrotechnic compositions of this invention may be used, for example, in flares, rocket motors, and secondary restraint systems ("air bag devices") in vehicles.

[0046] The following examples serve to explain embodiments of the present invention in more detail. These examples are not to be construed as being exhaustive or exclusive as to the scope of this invention.

EXAMPLES

Example 1

[0047] In a 50 ml Nalgene vial, 3.78 g (18.9 weight percent) of 6-micron phenolphthalein, 12.32 g (61.6 weight percent) of 15-micron potassium nitrate, and 3 g (15 weight percent) of 20-micron potassium perchlorate were dry blended for 1 min in a ~~mini paint~~mini-paint shaker. To these powders, 2.92 g of a 30.87% poly(vinyl acetate) in ethyl acetate (4.5 weight percent PVA dry weight) as well as 2.0 g of ethyl acetate were added. The ingredients were then mixed for one minute in the paint shaker followed by scraping the edges of the Nalgene container with a spatula and another minute of mixing in the paint shaker. A portion of the ethyl acetate was allowed to evaporate at ambient temperature in a fume hood with occasional stirring. The resulting paste was granulated sequentially through a 10, 16 and 30 mesh screen. The resulting granules were dried in a 73.9°C (165°F) oven and then sieved -40/+100 mesh. Ballistic performance was determined by igniting a 2 g sample with a hot wire in a 45 ee-losed~~cc~~ closed bomb. Humidity uptake data were

obtained by placing approximately 3 g of sample in aluminum ~~weigh~~weighing dishes in a closed container above a saturated sodium chloride solution at 21.1°C (70°F). Ballistic performance data are found in Table 1.

Example 2

[0048] A sample was made and tested ballistically in ~~an identical fashion~~a fashion ~~identical~~ to Example 1 but with 70-micron phenolphthalein. Humidity uptake data were obtained by placing an approximately 3 g of sample in ~~1-g~~1 g aluminum weighing pans in a closed container above a saturated sodium chloride solution at 21.1°C (70°F). The resulting ballistic and moisture uptake data are found in Table 1

Example 3

[0049] The same formulation as in Example 1 was scaled up to a 50 g ~~size~~size. In a 100 ml plastic vial, 9.45 g (18.9 weight percent) ~~of~~ 6-micron phenolphthalein, 30.8 g (61.6 weight percent) ~~of~~ 15-micron potassium nitrate, and 7.5 g (15 weight percent) ~~of~~ 20-micron potassium perchlorate were dry blended for 1 min in a ~~mini paint~~mini-paint shaker. To these powders, 7.3 g of a 30.87% poly(vinyl acetate) in ethyl acetate (4.5 weight percent PVA dry weight) as well as 5.0 g of ethyl acetate were added. The sample was mixed, granulated and tested ballistically as in Example 1 and for humidity uptake as in Example 2.

Example 4

[0050] Example three was repeated except for moisture uptake testing.

Examples 5-9

[0051] ~~Further 20 g~~Further, 20 g samples of the black powder substitute were mixed, granulated, dried and tested ballistically as in Example 1 and tested for moisture uptake as in Example 2. These formulations had varying levels of 6-micron phenolphthalein, 20-micron potassium perchlorate and ~~15 micron~~15-micron potassium nitrate. The amount of ethyl acetate and poly(vinyl acetate) dissolved in ethyl acetate remained the same. The formulation and testing data are summarized in Table 1.

Examples 10-12

[0052] Formulations were also prepared in which sulfur was an ingredient in addition to the ingredients listed in Example 2. The method of preparation varied such that the 70-micron phenolphthalein and the sulfur were ~~pre-blended~~preblended in a 125 ml plastic vial on the paint shaker in the presence of 0.635 cm (0.25 inch) diameter plastic beads before the blended material was added to the black powder substitute mix in a ~~20-g~~20 g Nalgene vial. Ballistic data should be compared to ~~those~~that for Example 2 in Table 1 since this formulation has phenolphthalein with a comparable particle size.

Example 13

[0053] This formulation containing sulfur was prepared and tested similarly to Examples ~~10-12~~10-12, but 6-micron phenolphthalein was used in the preparation thereof and thus their ballistics can be compared to those of Examples 1 and 3-9.

Example 14

[0054] In a 50 ml Nalgene vial, 0.9 g of 85-90% KOH were dissolved in 0.9 g of water. To this solution, 2.24 g of phenolphthalein were added and the ingredients were stirred until all of the phenolphthalein was converted to its dipotassium saltsalt, yielding a viscous violet syrup. To this syrup, 2.33 ml of 6 M nitric acid were added and this mixture was stirred until a white paste resulted. An additional 4.84 g of KNO₃ and 1.5 g of KClO₄ were added. The slurry was dried partially and granulated similarly to the paste in Example 1. Ballistic results and formulation percentages are found in Table 1.

Example 15

[0055] In a 50 ml Nalgene vial, 2.62 g of phenolphthalein were added to 0.5 g of a 70% water/30% ethanol solution. To this slurry, 1.34 g of a 30% aqueous KOH solution were added. The ingredients were ~~mixed~~mixed, yielding a violet-red ~~slurry~~slurry, and 11.98 g of KClO₄ were added. The slurry was dried and granulated to minus 12 mesh. The performance of the high flame temperature igniter was compared to that of a B/KNO₃ formulation in reusable hardware that

emulates an automotive safety bag driver's side gas generator (Figure 1). Specifically, the igniters were fired in reusable hardware designed to mimic the inflator of a driver's side automotive safety bag. The load of non-azide gas generant ("Metal Complexes For Use As Gas Generants"; Jerald C. Hinshaw, Daniel W. Doll, Reed J. Blau, Gary K. Lund; U.S. Patent Nos. 5,592,812 (1/14/97), 5,673,935 (10/7/97), 5,725,699 (3/10/98), and 5,735,118 (4/7/98)-(4/7/98)) utilized in both tests was 38 g. Moisture uptake data and the percentages of ingredients are summarized in Table 2.

Examples 16-21

[0056] Formulations were mixed similarly to that in Example 15. Binder was added at the same time as the oxidizer. Humidity uptake was determined as described in Example 2. The data are summarized in Table 2.

Table 1

BPS ID	H2PhPh Particle Size	Ave Slope (psi/msec)	Pmax (psi)	Time to Pmax (msec)	H2O Uptake, 75%RH > 18 h	% KClO4	% PVAc	% KNO3	% H2PHPh	% Sulfur
Black Powder Std	NA	251.92	1323.46	31.84	1.4					
Ex. 1	6	536.00	1687.50	22.95		15	4.5	61.6	18.9	0
Ex.2	70	210.50	1470.50	42.45	0.07	15	4.5	61.6	18.9	0
Ex.3	6	602.00	1741.00	21.20	0.03	15	4.5	61.6	18.9	0
Ex.4	6	569.50	1709.00	20.95		15	4.5	61.6	18.9	0
Ex.5	6	508.00	1705.00	23.60	0.07	12.5	4.5	64.2	18.8	0
Ex.6	6	74.50	1078.00	65.60	0.10	12.5	4.5	70.8	12.2	0
Ex.7	6	319.00	1472.00	33.15	0.23	10	4.5	70	15.5	0
Ex.8	6	283.00	1457.00	24.85	0.17	7.5	4.5	69.4	18.6	0
Ex.9	6	22.00	862.00	143.95	0.17	7.5	4.5	76	12	0
Ex.10	70	76.00	1182.50	82.30		5	4.5	61.5	19	10
Ex.11	70	107.50	1304.00	62.55	0.22	10	4.5	61.5	19	5
Ex.12	70	194.00	1448.00	54.03	0.20	15	4.5	51.2	19.3	10
Ex.13	6	322.50	1516.00	37.45		15	4.5	62	13.5	5
Ex.14	Ground <i>in-situ</i> <i>situ</i>	193.00	1434.50	31.85		15	0	62.6	22.4	0

Table 2

Ex.	Oxidizer	% Oxidizer	% Phenol-phthalein	% Dipotassium Salt of Phenol-phthalein	% Sulfur	Binder	% Binder	Moisture Uptake at 70°F, 75% RH, after 22 hours
15	KClO ₄	80.78	10.73	8.57	0	NA	0	1.02
16	KNO ₃	83	9.5	7.5	0	NA	0	1.65
17	KNO ₃	83	7.51	6.99	0	ethylcellulose	3.5	1.74
18	KNO ₃	73.4	12.24	1.36	10	ethylcellulose	3	0.56
19	KNO ₃	73.6	13.4	0	10	ethylcellulose	3	0.151
20	KNO ₃	73.8	12.96	1.44	10	Elvamide 8061	1.8	0.324
21	KNO ₃	74	14.2	0	10	Elvamide 8061	1.8	0.141

[0057] As seen from Table II, the inventive formulations had equivalent or superior ballistic properties equivalent or superior to conventional black powder and conventional black powder substitute compositions. Of the sulfur-free embodiments, the ballistic properties were especially good for Examples 1, 3-5, 7, and 8, in which the total oxidizer concentration was present in a range of 65 and to 80 weight percent and the phenolphthalein was present in a range of 13 to 22 weight percent. Example 2 used relatively large phenolphthalein particles of 70 microns. Examples 6 and 9 possessed more than 80 weight percent oxidizer. These factors lowered the ballistic performance, and in particular performance and, in particular, the average slope measurement, compared to Examples 1, 3-5, 7, and 8.

[0058] Table 2 demonstrates the high moisture uptake that a crystalline salt of phenolphthalein has in comparison to phenolphthalein in its organic crystalline state. The ratio of organic crystalline compound to salt has an inverse relationship to moisture uptake, i.e., as the ratio increased, the moisture uptake decreased.

[0059] The foregoing detailed description of the invention has been provided for the purpose of explaining the principles of the invention and its practical application, thereby enabling others skilled in the art to understand the invention for various embodiments and with various modifications as are suited to the particular use contemplated. This description is not intended to be exhaustive or to limit the invention to the precise embodiments disclosed. Modifications and equivalents will be apparent to practitioners skilled in this art and are encompassed within the spirit and scope of the appended claims.

ABSTRACT OF THE DISCLOSURE

A solid pyrotechnic composition having a flame temperature and exhibiting ballistic performance comparable to that of black powder, but which is preferably formulated to contain neither charcoal nor sulfur, is provided. A solid pyrotechnic composition having a flame temperature and ~~exhibit~~exhibiting ballistic performance comparable to that of boron/potassium ~~nitrate~~nitrate and that is preferably free of ~~boron~~boron is also provided.

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